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Accessory Metals Content of Commercial Titanium Mineral Concentrates

By Jack C. White and John B. Wright

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

kg	kilogram	ppm	part per million
pct	percent	st	short ton

ACCESSORY METALS CONTENT OF COMMERCIAL TITANIUM MINERAL CONCENTRATES

By Jack C. White[1] and John B. Wright[2]

ABSTRACT

This U.S. Bureau of Mines report assesses the resource potential of trace metals present in commercial Ti mineral concentrates. Metals of greatest interest are those defined as "strategic and critical" by the U.S. Congress in 1981. Metals of interest in Ti mineral concentrates are Cb, Cr, Ta, Th, U, V, and Zr.

Commercially available Ti mineral concentrates were studied. Characterization and analysis of major and minor constituents were performed by X-ray diffraction, neutron activation, inductively coupled plasma emission, atomic absorption, and classical wet chemical techniques.

Of the metals investigated, the Cb, Ta, and V content of some concentrates may be a significant potential resource, depending on their amenability to recovery.

[1]Metallurgist.
[2]Chemical engineer.
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INTRODUCTION

A goal of the U.S. Bureau of Mines is to maintain an adequate supply of minerals and metals to meet the Nation's economic and strategic needs. Metals considered to be "strategic and critical" are defined in the congressional handbook "U.S. Materials Import Dependence/Vulnerability."[3] To help maintain a supply of these metals, the Bureau is conducting research on extraction of the metals Cb, Cr, Ta, Th, U, V, and Zr from Ti chlorination waste.

Chlorination of Ti mineral concentrates in fluidized-bed reactors produces the chemical intermediate titanium tetrachloride ($TiCl_4$), used to manufacture all Ti metal and a major fraction of titanium dioxide (TiO_2) pigments. Most chlorination plants are arranged so that the waste materials generated during chlorination are composited into a single process stream that contains the critical metals listed previously.

This report describes the critical metals content of the Ti mineral concentrates used in chlorination plants. By characterizing the source materials, it should be possible to calculate the critical metals content of any chlorination waste for any blend of Ti mineral concentrates used as chlorinator feed. Most of the Ti feedstocks described here are commercial materials available in large tonnage. Descriptive information is presented in table 1.

Titanium mineral concentrates used in chlorination plants are produced mostly from beach sand deposits by physical separation (beneficiation) processes. The Ti minerals of interest are rutile (TiO_2) and ilmenite ($FeO \cdot TiO_2$) and alteration products of ilmenite, often consisting mostly of pseudorutile ($Fe_2O_3 \cdot 3TiO_2$). Altered beach sand ilmenites also are used as feedstock for manufacturing synthetic rutile or rutile substitutes used in chlorination plants. High-Ti slag, made by carbothermic reduction of altered beach sand, also is used in some chlorination plants.

This study assesses the resource potential of critical metals contained in the Ti mineral concentrates entering the chlorination process. The resource potential was determined by comparing the quantity of each critical metal with U.S. demand for that metal.

Table 1.—Source and principal minerals of commercial Ti mineral concentrates

Source	Sample	Principal minerals
Australia:		
New South Wales:		
Newcastle	4	Rutile.
	14	Ilmenite, pseudorutile.
	15	Ilmenite, rutile.
Queensland: Brisbane	5	Rutile.
	12	Ilmenite.
Western Australia:		
Capel	10	Synthetic rutile.[1]
	13	Ilmenite, pseudorutile.
Eneabba	3	Rutile.
	11	Complex rutile substitute.[2]
	21	Pseudorutile, rutile.
Brazil: São Paulo	6	Rutile.
	22	Ilmenite, pseudorutile.
Canada:		
Quebec: Allard Lake	27	Pseudobrookite (slag).
India:		
Chavara	8	Rutile, anatase.[3]
	18	Ilmenite, pseudorutile, rutile.
Manavalakurichi	16	Ilmenite, pseudorutile.
Orissa	17	Ilmenite.
Sierra Leone: Mogbwemo	2	Rutile.
South Africa, Republic of:		
Richards Bay	1	Rutile.
	26	Pseudobrookite (slag).
Sri Lanka: Pulmoddai	9	Rutile.
	19	Ilmenite, pseudorutile.
United States:		
Colorado: Gunnison Co	28	Perovskite.
Florida:		
Green Cove Springs	7	Rutile.
	23	Pseudorutile, rutile.
	24	Pseudorutile, rutile.
Starke	25	Pseudorutile, rutile.
New York: Tahawus	20	Ilmenite.

[1]Synthetic rutile produced by Kerr-McGee Corp.

[2]Rutile substitute manufactured at Capel from altered ilmenite mined near Eneabba on the southwest coast.

[3]Q-grade.

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[3]U.S. House of Representatives. A Congressional Handbook on U.S. Materials Import Dependence/Vulnerability. Committee on Banking, Finance, and Urban Affairs, Subcommittee on Economic Stabilization. 97th Congr., 1st sess., Committee Print 97-6, Sept. 1981, 405 pp.

MINERALOGICAL CHARACTERIZATION AND CHEMICAL ANALYSIS

The Ti mineral concentrates were characterized and analyzed to determine both mineralogical and chemical compositions. Analyses by the Bureau were performed by X-ray diffraction, inductively coupled plasma (ICP) emission, atomic absorption (AA), and classical wet chemical methods. Neutron activation and radiometric analyses were done by the Oregon State University Radiation Center Laboratory.

MINERALOGICAL COMPOSITIONS

The bulk mineralogical compositions of the concentrates were determined by X-ray diffraction. Rutile concentrates listed in table 2 consist principally of the mineral rutile, the high-pressure, high-temperature polymorph of TiO_2. Rock ilmenites and some beach ilmenites (table 3) have the ilmenite crystal structure and composition ($FeO \cdot TiO_2$), whereas beach ilmenites that have been altered by long exposure to weathering conditions consist in part or entirely of the mineral pseudorutile ($Fe_2O_3 \cdot 3TiO_2$). Alteration from ilmenite to pseudorutile changes the Fe-Ti molecular ratio from 1:1 to 2:3, thereby increasing the TiO_2 content appreciably. Pseudorutile is the preferred starting material for two commercial synthetic rutile manufacturing processes.

Synthetic rutile is produced from pseudorutile by Kerr-McGee Corp.[4] of Mobile, AL, by means of a modified Benelite Process. The synthetic product consists of microcrystalline aggregates of rutile that are essentially the same shape and size as the original pseudorutile sand grains. A rutile substitute is produced by Associated Minerals of Capel, Western Australia, by the Western Titanium Process from pseudorutile concentrates mined at Eneabba, Western Australia. The rutile substitute consists of a complex mixture of rutile and Ti suboxide species, again of the size and shape of the original sand grains.

[4]Reference to specific products or manufacturers does not imply endorsement by the U.S. Bureau of Mines.

Table 2.—Analyses of rutiles and synthetic rutiles

Sample	Ca, pct	Cb, pct	Ce,[1] ppm	Co,[1] ppm	Cr,[1] ppm	Fe, pct	Hf,[1] ppm	Mg, pct	Mn,[1] pct	Sc,[1] ppm	Si, ppm	Ta,[1] ppm	Ti, pct	V,[1] ppm	Zr,[1] ppm
RUTILES															
1	0.06	0.064	90	1.5	740	0.86	310	0.05	0.011	61	0.95	170	57.3	2,210	1,180 ±400
2	<.05	.02	80	1.4	1,600	.85	210	.04	.0060	17	.31	56	59.3	3,100	8,600 ±200
3	<.05	.04	38	.6	990	.62	200	.02	.0075	25	.07	210	59.7	2,890	8,200 ±300
4	<.05	.028	26	.8	1,130	.34	180	.11	.0039	37	.02	220	59.8	3,100	6,900 ±300
5	<.05	.036	48	1.4	1,490	.69	190	.11	.0055	58	.39	190	57.7	2,880	7,400 ±400
6	<.05	.042	220	.6	640	.46	390	.02	.0028	33	.46	220	57.0	2,130	14,400 ±300
7	<.05	.069	<32	ND	630	1.26	47	.02	.025	45	<.01	360	59.5	1,390	ND
8	<.05	.053	ND	1.3	1,420	.88	260	.07	.0028	26	.36	550	57.4	2,390	8,600 ±300
9	<.05	.038	80	.8	1,130	.59	210	.03	.0052	21	.02	180	59.8	2,780	8,000 ±200
SYNTHETIC RUTILES															
10	<0.05	0.027	ND	1.7	670	2.03	20	0.04	0.031	63	0.45	140	58.4	820	1,060 ±200
11	<.05	.038	330	18	1,840	3.68	27	.24	1.24	290	.23	180	57.0	1,200	ND

ND Not determined.

[1]Analysis by neutron activation method at Oregon State University Radiation Center Laboratory. All other analyses by the Bureau.

Table 3.—Analyses of ilmenites, altered ilmenites, slags, and perovskite

Sample	Ca, pct	Cb, pct	Ce,[1] ppm	Co,[1] ppm	Cr,[1] ppm	Fe, pct	Hf,[1] ppm	Mg, pct	Mn,[1] pct	Sc,[1] ppm	Si, ppm	Ta,[1] ppm	Ti, pct	V,[1] ppm	Zr,[1] ppm
ILMENITES AND ALTERED ILMENITES															
12 . .	<0.05	0.008	280	89	7,900	32.0	110	0.70	1.03	65	0.77	32	31.1	950	4,800 ±200
13 . .	<.05	.006	90	45	230	28.6	14	.15	1.07	79	.22	69	35.5	750	690 ±180
14 . .	<.05	.012	<40	141	49,000	20.5	44	3.57	3.80	88	.19	92	26.1	ND	1,900 ±200
15 . .	<.05	.009	150	90	23,000	25.6	24	1.64	1.01	124	.01	78	23.0	1,270	ND
16 . .	.08	.002	ND	71	630	28.2	29	.57	.28	66	.41	93	33.7	1,120	1,100 ±200
17 . .	.06	.013	ND	88	440	35.2	16	.44	.43	61	.21	61	31.3	1,160	ND
18 . .	.08	.019	ND	59	930	23.6	112	.57	.12	84	.22	87	37.6	490	5,300 ±300
19 . .	.26	.012	350	72	840	27.5	66	.55	.64	104	.53	37	33.8	1,300	3,300 ±300
20 . .	.23	<.01	ND	220	140	35.3	6	1.44	.33	40	.50	2.4	29.0	610	ND
21 . .	.08	.017	900	55	1,680	23.5	61	.18	.77	88	.58	144	37.0	910	2,800 ±300
22 . .	<.05	.014	240	52	370	26.6	22	.30	.69	118	.25	71	35.1	990	950 ±250
23 . .	.16	.012	90	38	820	21.6	8	.16	1.04	53	.01	78	39.6	550	ND
24 . .	.34	.010	400	31	720	17.6	13	.16	.77	63	.31	141	41.1	640	860 ±250
25 . .	.13	.012	100	36	490	20.2	34	.18	.81	56	.40	139	36.9	630	1,700 ±200
SLAGS AND PEROVSKITE															
26 . .	0.08	0.018	240	1.7	3,030	7.98	46	0.64	1.32	109	0.72	56	53.5	2,010	2,200 ±200
27 . .	.27	.008	<6	9.0	1,320	9.02	15	3.12	.18	85	.96	5	49.1	2,880	720 ±170
28 . .	21.5	.051	ND	20	400	3.76	11	1.49	.085	14	1.44	270	32.6	160	4,000 ±300

ND Not determined.

[1]Analysis by neutron activation method at Oregon State University Radiation Center Laboratory. All other analyses by the Bureau.

High-Ti slags, which are produced by carbothermic reduction of ilmenite, consist mostly of pseudobrookite, a crystalline structure that tolerates large amounts of impurities in solid solution. Titanium slag produced from beach ilmenite at Richards Bay, Republic of South Africa, reportedly is suitable for chlorination in some plants. Slag produced from rock ilmenite at Sorel, Quebec, Canada, is higher in impurities and reportedly is used as a blending feedstock in some chlorination plants, but its principal use is in sulfate route pigment production.

CHEMICAL ANALYSIS

Bureau analyses were performed on portions of the 1-kg samples supplied by the producers. The samples were taken into solution with sodium peroxide fusion and analyzed as follows:

Cb . . . . . Separation and concentration by wet methods, determination by ICP
Fe, Ti . . . Titrametric wet methods
Ca, Mg . . Separation by wet methods, determination by AA
Si . . . . . Gravimetric wet method

Tantalum, in the low concentrations contained in these samples, is near the detectability limits of ICP analysis. Because Ta was of special interest in this study, neutron activation analysis was used for more accurate results. Other metals determined by the neutron activation method were Ce, Co, Cr, Hf, Mn, Sc, V, and Zr. Uranium and thorium were analyzed by a radiometric method. Primary radiometric standards were supplied by the New Brunswick Laboratory, U.S. Department of Energy. Neutron activation and radiometric analyses were performed by the staff of the Oregon State University Radiation Center. Analytical data are presented in tables 2, 3, and 4.

Table 4.—Analyses of Ti concentrates for U and Th by the radiometric counting method[1]

Sample[2]	U-609 ppm	U-609 Error,[3] pct	Th-583 ppm	Th-583 Error,[3] pct	Sample[2]	U-609 ppm	U-609 Error,[3] pct	Th-583 ppm	Th-583 Error,[3] pct
1	50.45	0.5	55.55	1.6	17	3.83	3.3	80.11	1.1
4	44.95	.5	5.57	10.9	18	40.15	.8	497.47	.7
5	44.92	.5	15.78	4.2	19	16.30	1.1	110.45	1.0
6	44.59	.6	75.66	1.3	20	.04	41.5	.17	57.5
7	19.46	.8	17.92	3.0	22	13.36	1.5	208.10	.8
8	84.25	.4	28.56	2.9	23	13.48	1.1	42.65	1.6
10	6.60	2.5	60.44	1.5	24	27.61	.8	120.81	1.0
12	8.30	1.6	63.32	1.1	25	9.21	1.4	39.23	1.6
13	6.11	2.2	91.74	1.0	26	6.06	2.2	55.58	1.4
14	12.03	1.0	25.43	2.1	27	.38	11.5	1.16	17.4
15	8.82	1.4	30.87	1.8	28	54.12	.6	180.91	.9
16	23.99	1.1	403.09	.7					

[1]Weights calculated using Ra-226 photopeaks for U and Th-232 photopeaks for Th.
[2]Unlisted samples were of insufficient size for analysis by this method.
[3]Represents statistical counting error only.

DISCUSSION

An overview of the resource potential of critical metals contained in Ti mineral concentrates was provided by calculations based on the analytical data in tables 2 and 3 and on U.S. metal consumption data published in the Bureau's "Minerals Yearbook" (1984).[5] The calculated values express the metals content of Ti mineral concentrates as a percentage of U.S. demand for Cr, Cb, Ta, V, and Zr. For these calculations, each Ti concentrate was assumed to supply the entire U.S. demand for Ti (table 5). A sample calculation also is presented. Columbium, tantalum, and vanadium are contained in substantial quantities, amounting to one-fourth to one-third or more of U.S. demand in some concentrates. Zirconium is present in less significant amounts, and Cr (except for samples 14 and 15) is present in insignificant quantities. A significant fraction of U.S. demand for Cb, Ta, and V could potentially be satisfied by recovery from Ti concentrates; however, the concentrates are a dilute source.

Three factors, however, cause the Cb, Ta, and V contents to be of interest. First, in averaging the analyses of the nine rutile samples listed in table 2 (samples 1 through 9), it is apparent that Cb, Ta, and V are present in much higher concentrations in rutile than in average crustal rocks (table 6). In rutile, the Ta concentration ratio is much higher than the Cb or V ratio. In Green Cove Springs altered ilmenite (sample 24) and Sorel slag (sample 27), the concentration ratios differ markedly from those of rutile: higher for Cb and lower for Ta, especially for Ta in slag. The ratio for V is higher in the slag.

[5]Lynd, L. E., and R. A. Hough. Titanium. Ch. in BuMines Minerals Yearbook 1984, v. 1, pp. 913-926.

Table 5.—Content of critical metals in Ti mineral concentrates expressed as percentage of U.S. demand[1] (assuming 100-pct recovery)

Sample	Cb	Cr	Ta	V	Zr
1[2]	48	0.23	25	45	18
2	14	.47	8.0	61	12
3	28	.29	30	56	12
4	20	.33	31	60	9.8
5	27	.45	28	60	11
6	31	.20	33	43	22
7	49	.19	51	27	1.4
8	39	.43	81	48	13
9	27	.33	26	54	11
10	20	.20	20	16	1.5
11	28	.57	27	24	.5
12	11	4.4	8.7	35	13
13	7.0	.11	16	25	1.7
14	20	33	30	67	6.2
15	17	18	29	64	1.1
16	28	.33	23	39	2.8
17	18	.25	17	43	.5
18	21	.43	20	15	12
19	15	.43	9.3	45	8.3
20	<15	.08	.70	24	.3
21	20	.80	33	29	6.5
22	17	.18	17	33	23
23	13	.36	17	16	.64
24	10	.31	29	18	1.8
25	14	.23	32	20	3.9
26	14	1.0	8.9	43	3.5
27	6.9	.48	.86	68	1.2
28	66	.21	70	5.7	10

[1]Metal consumption figures from the Bureau's "Minerals Yearbook" (1984) in short tons: Cb, 1,300; Cr, 314,820; Ta, 650; Ti, 552,400; V, 4,761; Zr, 64,740.
[2]Sample calculation for Ta in sample 1: Given: Ti consumption (1984) = 552,400 st, Ta analysis = 170 ppm, Ti analysis = 57.3 pct (from table 2); then: [[(552,400/0.573) X 170 X 10^{-6}]/650 st Ta] X 100 = 25.214 pct of annual demand.

Table 6.—Concentration of critical metals in average rutile, altered beach ilmenite, and slag, compared with average crustal rock

Critical metal	Average crustal rock,[1] ppm	Average rutile		Beach ilmenite		Sorel slag	
		ppm	Ratio	ppm	Ratio	ppm	Ratio
Cb ...	20	430	21.5	1,000	50	800	40
Ta ...	2	240	120	141	70	5	2.5
V	135	2,541	19	640	4.8	2,800	21

[1]Source: Mason, B., and C. B. Moore. Principles of Geochemistry. Wiley, 4th ed., 1982, pp. 46-47.

Second, removing TiO_2 by chlorination causes additional concentration of the remaining metals. Because of the high TiO_2 content of rutile, the concentration during chlorination is higher than it is for ilmenites or slag. For example, the average TiO_2 content of the nine rutile samples in table 2 is 97.75 pct; the average chlorination concentration factor for these rutiles is $1/(1 - 0.9775) = 44$. Chlorination concentration factors are extremely sensitive to small amounts of impurities in rutile. Concentration of metals during chlorination of ilmenite and slag is much lower, mostly due to their higher Fe content. For rutile, the products of natural concentration and chlorination concentration factors are remarkably large numbers, especially for Ta (table 7). In contrast, combined concentration factors for ilmenite and slag are much lower than for rutiles. Rutile, therefore, is of greatest interest as a potential source of critical metals.

Table 7.—Concentration factors for Cb, Ta, and V

Concentration factor	Cb	Ta	V
Natural:			
Rutile	21.5	120.0	19.0
Ilmenite ...	50	70	4.8
Slag	40	2.5	21
Chlorination:			
Rutile	44	44	44
Ilmenite ...	3.18	3.18	3.18
Slag	5.55	5.55	5.55
Combined:			
Rutile	946	5,280	836
Ilmenite ...	159	223	15.3
Slag	222	13.9	117

A third favorable aspect of chlorination waste is that the Cb, Ta, and V may be in acid-soluble form as chlorides, which should provide a favorable starting point for separation and recovery.

Analysis of a rutile-derived chlorination waste may be calculated assuming complete chlorination of the rutile and no dilution of the waste during the chlorination process. Recalculating the concentration factor for rutile sample 1 (a sample that is lower than average in TiO_2) and multiplying by the analyses in table 2 provide the data of table 8. The calculated analysis indicates a complex mixture of metals that may prove difficult to separate into marketable products. An additional potential problem is the Th and U content, which may be high enough to be of concern in material processing and disposal. The Th content of Ti mineral concentrates varies over a wide range—from less than 1 ppm in rock ilmenite to almost 500 ppm in one beach sand ilmenite (table 4). Presumably, a significant fraction of the Th is contained as discrete grains of monazite, a rare-earth phosphate mineral that may contain as much as 8 pct Th. Physical separation of the monazite from the concentrates before chlorination appears to be the preferable means of reducing the Th content of chlorination wastes.

Table 8.—Calculated analyses of waste from chlorination of rutile sample 1, percent [1]

Ca	1.36	Mn ...	0.45
Cb	1.45	Sc ...	.14
Ce	.20	Si	21.6
Co	.0034	Ta ...	.39
Cr	1.7	Th ...	.13
Fe	19.5	U	.11
Hf	.70	V	4.76
Mg	1.13	Zr ...	22.7

[1]Sample calculation: 57.3 pct Ti X (79.9/47.9) = 95.6 pct TiO_2, $1/(1 - 0.956) = 22.7$ (chlorination concentration factor). Ca analysis from table 2 = 0.06 X 22.7 = 1.36 pct.

An additional consideration is that particles of Ti minerals and coke, quartz, silicates, and refractory chlorinator lining material blow out of the fluidized-bed chlorinator. These particles would dilute the calculated chlorinator waste (table 8). The situation is further complicated, as shown by Paige, Mussler, and Elger,[6] who found that unreacted rutile, coke, and silicates can be recovered from chlorination waste by simple physical separation equipment, presumably leaving the critical metals of interest in relatively dilute mixtures.

[6]Paige, J. I., R. E. Mussler, and G. W. Elger. Physical Benefication of Titanium Plant Solid Wastes: Recovery of Titanium Minerals and Coke. BuMines RI 8737, 1982, 23 pp.

CONCLUSIONS

1. Data presented above will serve as a guide in considering Ti mineral concentrates as potential sources of some critical metals.

2. Columbium, tantalum, and vanadium appear to be of the greatest economic significance.

3. The high natural concentrations of Cb, Ta, and V in rutile, multiplied by the chlorination concentration ratio, provide relatively high concentrations of these metals in chlorination waste.

4. Separations to provide marketable products from the complex mixture of metals in the chlorination waste may be difficult.

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